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APPLICATION NUMBER: ***60/510,983***
FILING DATE: ***October 14, 2003***
RELATED PCT APPLICATION NUMBER: ***PCT/US04/33915***

Certified by

Jon W Dudas

Acting Under Secretary of Commerce
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PTO/SB/16 (10-01)
Approved for use through10/31/2002. OMB 0651-0032
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. EV178871405US

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
J. Donald	Carruthers	Fairfield, CT
Jose I.	Arno	Brookfield, CT

☐ *Additional inventors are being named on the _______ separately numbered sheets attached hereto*

22581 U.S. PTO 60/510983

TITLE OF THE INVENTION (500 characters max)

H2 GENERATION

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

☑ Customer Number 25559 *Type Customer Number here* → *Place Customer Number Bar Code Label here*

OR

☐ Firm or Individual Name	Margaret Chappuis				
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ENCLOSED APPLICATION PARTS *(check all that apply)*

☑ Specification *Number of Pages* 11
☑ Drawing(s) *Number of Sheets* 2
☐ Application Data Sheet. See 37 CFR 1.76
☐ CD(s), Number
☐ Other (specify)

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☐ Applicant claims small entity status. See 37 CFR 1.27.
☐ A check or money order is enclosed to cover the filing fees
☑ The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 50-0860
☐ Payment by credit card. Form PTO-2038 is attached.

FILING FEE AMOUNT ($): $160.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.
☑ No.
☐ Yes, the name of the U.S. Government agency and the Government contract number are: ____________

Respectfully submitted,

SIGNATURE Margaret Chappuis

Date 10/14/2003

TYPED or PRINTED NAME Margaret Chappuis

REGISTRATION NO. *(if appropriate)* 45,735

TELEPHONE 203-794-1100

Docket Number: ATMI-682-PRV

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

PTO/SB/17 (10-03)
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☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT ($) 160

Complete if Known	
Application Number	
Filing Date	
First Named Inventor	J. Donald Carruthers
Examiner Name	
Art Unit	
Attorney Docket No.	ATMI-682-PRV

METHOD OF PAYMENT *(check all that apply)*

☐ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None

☑ Deposit Account:

Deposit Account Number: 500860

Deposit Account Name: Advanced Technology Mater

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FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
1001	770	2001	385	Utility filing fee	
1002	340	2002	170	Design filing fee	
1003	530	2003	265	Plant filing fee	
1004	770	2004	385	Reissue filing fee	
1005	160	2005	80	Provisional filing fee	160

SUBTOTAL (1) ($) 160

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

		Extra Claims	Fee from below	Fee Paid
Total Claims	-20** =		x	=
Independent Claims	- 3** =		x	=
Multiple Dependent				=

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description
1202	18	2202	9	Claims in excess of 20
1201	86	2201	43	Independent claims in excess of 3
1203	290	2203	145	Multiple dependent claim, if not paid
1204	86	2204	43	** Reissue independent claims over original patent
1205	18	2205	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) ($)

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FEE CALCULATION (continued)

3. ADDITIONAL FEES

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1051	130	2051	65	Surcharge - late filing fee or oath	
1052	50	2052	25	Surcharge - late provisional filing fee or cover sheet	
1053	130	1053	130	Non-English specification	
1812	2,520	1812	2,520	For filing a request for *ex parte* reexamination	
1804	920*	1804	920*	Requesting publication of SIR prior to Examiner action	
1805	1,840*	1805	1,840*	Requesting publication of SIR after Examiner action	
1251	110	2251	55	Extension for reply within first month	
1252	420	2252	210	Extension for reply within second month	
1253	950	2253	475	Extension for reply within third month	
1254	1,480	2254	740	Extension for reply within fourth month	
1255	2,010	2255	1,005	Extension for reply within fifth month	
1401	330	2401	165	Notice of Appeal	
1402	330	2402	165	Filing a brief in support of an appeal	
1403	290	2403	145	Request for oral hearing	
1451	1,510	1451	1,510	Petition to institute a public use proceeding	
1452	110	2452	55	Petition to revive - unavoidable	
1453	1,330	2453	665	Petition to revive - unintentional	
1501	1,330	2501	665	Utility issue fee (or reissue)	
1502	480	2502	240	Design issue fee	
1503	640	2503	320	Plant issue fee	
1460	130	1460	130	Petitions to the Commissioner	
1807	50	1807	50	Processing fee under 37 CFR 1.17(q)	
1806	180	1806	180	Submission of Information Disclosure Stmt	
8021	40	8021	40	Recording each patent assignment per property (times number of properties)	
1809	770	2809	385	Filing a submission after final rejection (37 CFR 1.129(a))	
1810	770	2810	385	For each additional invention to be examined (37 CFR 1.129(b))	
1801	770	2801	385	Request for Continued Examination (RCE)	
1802	900	1802	900	Request for expedited examination of a design application	

Other fee (specify) ____________

*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) ($)

SUBMITTED BY		(Complete *(if applicable)*)	
Name *(Print/Type)*	Margaret Chappuis	Registration No. *(Attorney/Agent)* 45,735	Telephone 203-794-1100
Signature	Margaret Chappuis		Date 10/14/2003

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This collection of information is required by 37 CFR 1.17 and 1.27. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Docket No.: ATMI-682-PRV
Customer ID No.: 25559

In re application of: J. Donald Carruthers, et al.

TITLE : **H2 GENERATION**

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The following papers are enclosed:

Provisional Application for Patent Cover Sheet (1 pg)
Fee Transmittal (1 pg) (In Duplicate)
Specification (11)
2 Sheets of Drawings (Figs. 1, 2 and 6)

Docket Number: 682

UNITED STATES PROVISIONAL PATENT APPLICATION

OF

J. DONALD CARRUTHERS

AND

JOSE I. ARNO

FOR

H_2 GENERATION

EXPRESS MAIL CERTIFICATE OF MAILING

Express Mail Label Number: EV178871405US

Date of Deposit: October 14, 2003

H_2 GENERATION

Background

In the January 2003 State of the Union Address, President Bush reaffirmed the Nation's commitment to energy independence and an improved environment by proposing $1.2 billion in research funding for hydrogen and fuel cell technologies over the next five years. While hydrogen production and fuel cell technologies to support this goal are well advanced, the greatest challenge ('Grand Challenge') is undoubtedly the need for a cost-effective, on-board hydrogen storage system that will meet the DOE minimum vehicle range of 300 miles within the weight and volume constraints of the vehicle. DOE emphasizes that this is the greatest challenge, since no hydrogen storage technology available today can meet the DOE cost and performance targets.(1)

Of the technical challenges facing this goal, on-board storage of hydrogen is perhaps the most formidable. Although hydrogen can be stored in several ways, e.g on a solid adsorbent, as a cryogenic liquid, as a compressed gas, or even as a solid chemical hydride, significant barriers must be overcome with each of these methods before the targeted goals can be achieved.

The problem of hydrogen storage is multifaceted. Various approaches have been tried: adsorption of H2 on inert solids, storing liquid petroleum or methanol followed by reforming to H2 , and decomposition of solid hydrides. Conventional adsorption methods and materials have been shown to be completely inadequate. Reports in 1997 of high hydrogen adsorption levels on carbon nanotube adsorbents appeared to supply an answer(2, 4), but attempts to repeat the work were disappointing(3, 5). McEnaney reviewed the state of the art in a review paper in 2003(6) and concluded that numerous claims had been made, but there was little convincing evidence that hydrogen can be adsorbed at the levels required. Indeed, should hydrogen adsorb at the levels originally claimed(2), the specific gravity of hydrogen at room temperature within the carbon nanotube would have to exceed that of solid hydrogen by a factor of 2.88(7); quoting the author of that work: "*...such a supercompacted form of hydrogen is strange to contemporary physics...*". Other theoretical studies arrived at the same conclusion(8) .

Finally, at a recent international meeting of carbon scientists (Carbon 2003, Oviedo, Spain), there was an open panel discussion of hydrogen adsorption on carbon nanotubes, in which the question was posed to the audience of 150 people whether anyone had convincing evidence that the levels of hydrogen adsorption necessary to meet DOE targets could be reached. It is critical that alternative approaches be considered as well.

Hydrogen can be stored as a chemically-bonded hydride, and much work is underway at National Laboratories(9) and industrial concerns(10) to demonstrate such technology. This work centers on the use of solid hydrides of the type NaAlH4 doped with certain activating elements such as Ti. Complex hydrides, of the form Mg(AlH4)2•AlH6(11) are also under investigation. These technologies, while promising, introduce other challenges, such as the necessary change to solids handling and away from fluids handling in the energy distribution system, the poor gravimetric energy density of the fuel,(6) and the fact that the solid hydrides must be heated to relatively high temperatures in order to release hydrogen.

Hydrogen production *via* reforming of methanol and/or methane has received some attention.(12) Adsorbed Natural Gas (ANG) powered vehicles were evaluated extensively in the 1990's,(13) but the use of ANG as a source of hydrogen would require a similar level of technology as proposed for petroleum fuel processing for fuel cell powered vehicles, and would still generate large amounts of CO2.

The military has identified the need for small portable electric power supplies. The U.S. infantryman, for example, has become extremely efficient through the use of high tech. devices; e.g. devices which provide him with night vision capability and now I.R. 'vision'. These devices however require increasing amounts of portable electric power. Currently-available battery packs are both heavy and unwieldy and function for only a few hours at a time before requiring recharge. Re-charging devices using fuel cells are under development but these require hydrogen as fuel, supplied either from a compressed gas cylinder or more usually, by catalytic treatment of a liquid fuel such as methanol. One downside to the use of methanol is the fact that the catalytic treatment process uses some portion of the fuel in its conversion to hydrogen thereby reducing its efficiency. This approach is still quite attractive with the foot-soldier carrying refill

cartridges of methanol. The other option of carrying a high pressure, heavy compressed hydrogen gas cylinders is not acceptable.

Brief Description of the Drawings

Figure 1: Conceptual schematic of hydrogen storage via silane adsorption and regeneration.

Figure 2: Silane decomposition to H_2 & Si on untreated carbon (various tests) and H_3PO_4-treated carbon.

Figure 3: Silane adsorption/desorption isotherms at 294.2°K

Detailed Description

The following United States Patents are incorporated herein in their entirety, by reference in their entirety. United States Patents 5518528 and 6089027.

The invention described here relates to an alternative to conventional hydrogen storage methods. In essence, the invention we propose has three separate stages:

A.- Safe storage of a hydride material in a reduced pressure package
B.- Method to decompose the hydride in order to generate H2
C.- Ability to regenerate (*in* or *ex-situ*) the left-over metal back to the hydride

Note that the essential invention is a combination of steps (A) and (B); The last regeneration step (C)is not necessary but closes the materials lifecycle loop. The three stages are described next in addition to systems integration and examples of materials suitable for H2 generation.

Safe Hydride Gas Storage: Many hydride gases are toxic posing environmental or human safety hazards. Therefore, a major barrier for accepting the concept of in-situ generation of hydrogen frrm a hydride precursor are concerns over accidental high pressure gas release. Extensive investigations have been made by ATMI(14) to demonstrate the value of the Safe Delivery System. Tests were conducted by remotely

opening a conventional phosphine cylinder valve located in a secure cabinet and measuring the maximum gas evolution rate during the release period. The release rate of phosphine from the conventional high pressure cylinder attained levels as high as 29,000 ppm/minute. The maximum release rate reached by opening the valve of a SDS™ cylinder was only 480 ppb/minute. These tests and nearly 10 years of perfectly safe performance have convinced the semiconductor industry that these gases can be handled safely in a routine manner. As many as 40,000 SDS™ cylinders are currently in use, worldwide. In addition to the aforementioned safety advantages of storing gases in the adsorbed phase, it has been recently discovered that they can reduce the risk of deflagration when storing deflagration-prone gases (such as germane). Because of the "unstable" nature of some of the hydrides, adsorbents may need to be passivated to prevent premature or uncontrolled decomposition. For example, boric acid treatment is a well-known method for oxidation suppression in carbon materials, (15) where it is believed to involve bonding of (BO3)n to the edge of the {101*l*} face of graphite. We thus believe that the passivating effect observed in our own data is good evidence for the importance of *carbon edge-site chemistry* in hydride decomposition. The following are potential features of the hydride storage system:

- The characteristics of the adsorbent are the same of the ones described in the SDS or SAGE patents. Pore size distribution will be optimized to yield optimum storage and desorption rates. The can be carbon or zeolite based. In addition, the media can be pelletized, beaded or a solid monolith block.
- Another gas storage method that could be suitable for risk reduction in this invention, is the use of a mechanical regulator (such as ATMI's VAC' package) inside the vessel to prevent high-pressure gas release.
- Moreover, additional safety advantages can be achieved using a combination of adsorbent and mechanical regulator technologies.
- The pressure vessel storing the hydride can be sub-atmospheric or at reduced pressures compared to conventional storage but above atmospheric pressures.
- In yet another version of this invention, gas is stored in an adsorbent and a check valve prevents the potentially dangerous situation where air back diffuses to the container.

Hydride Decomposition:

We propose a novel approach to hydrogen storage. A recent discovery at ATMI has demonstrated that silane gas (SiH_4), stored as an adsorbed-phase in a nano-composite medium at sub-atmospheric pressures, can self-decompose at a near constant rate, producing H_2 and solid silicon. This decomposition occurs at room temperature without the need for external heat *or elevated pressure.* This exciting, new hydrogen storage concept involves, therefore, the release of hydrogen *via* the decomposition of a hydride gas stored in a nano-composite, adsorbed-phase vessel according to the reaction:

*A*xHy (adsorbed gas-phase) x*A*(s) + y/2 H2 (g)

where *A* denotes an element capable of forming a gaseous hydride.

The thermodynamic tendency for this reaction to occur at room temperature is indicated by the Gibbs free energy of formation of the hydride at 298K, ΔG_f. The decomposition of certain hydrides are more thermodynamically favored than others. Stibine (SbH_3, ΔG^o_f = +147.8 kJ/mole), germane (GeH_4, ΔG^o_f = +113.4 kJ/mol), diborane (B_2H_6, ΔG^o_f = +86.7 kJ/mol), and silane (SiH_4, ΔG^o_f = +56.9 kJ/mole) are gaseous hydrides which, subject to kinetic limitations, can spontaneously decompose at room temperature. On the other hand, the decomposition of methane (CH_4, ΔG^o_f = -50.84 kJ/mol) is very unfavorable under these conditions. Of these gases, silane stands out as the leading candidate based on safety and abundance considerations.

Decomposition rates can be modulated using the following methods:

- Heating the vessel to increase kinetic decomposition rates.
- Pressurizing the vessel to increase kinetic rates
- Modify the surface sites of the carbon to catalyze decomposition: There is the possibility of developing higher-rate decomposition catalysts by increasing the number of active edge sites on carbon. Data developed at ATMI showed *enhanced* decomposition rates after doping with phosphoric acid, implying a synergist mechanism involving carbon edge sites and phosphorous. Overall, we believe that our

ability to systematically manipulate both edge-site concentration and the type, amount, and dispersion of inorganic dopants, there is great potential to find an effective catalyst formulation for rapid, on-demand hydrogen production from the silane source. Figure 1 indicates the decomposition of silane as a function of carbon site functionalization.

- Use some of the hydrogen being generated to cool or heat up the vessel to slow down or accelerate H2 generation.

Material Regeneration:

Once the hydride has been fully utilized to generate hydrogen, the non-gaseous metal is left in the vessel. That metal can be recycled back to the hydride form in order to complete the material lifecycle. This can be more effectively accomplished in or ex-situ. Unlike current reforming technologies used to generate hydrogen which liberate the second element into the environment, (usually carbon as carbon oxides), this technology aims to confine the other element (Si) for conversion back to a hydrogen-containing species. From the thermodynamic point of view, the enthalpy required for formation of the silane is +34.3 kJ/mole while the heat of combustion of the generated hydrogen reaches -483.6 kJ, a net overall benefit of -449 kJ. Methods for hydride regeneration include:

- Use hydrogen and heat/and or pressure to covert the metal back to the hydride
- Use another hydride with the ability to donate some of its hydrogen atoms to regenerate the leftover metal. For example, a higher order borane (such as decaborane) could donate some of its hydrogens to react with boron and form diborane. Energy balances will dictate best alternatives.
- Use a halogen gas to extract the metal to generate metal halides; as a second stage, displace the halogen atoms via reaction with H2 (with heat, catalysts, or pressure) to form the hydride.

For example using silicon,

Step 1: $Si + 2Cl_2 = SiCl_4$

Step 2 $SiCl_4 + 2H_2 = SiH_4 + 2Cl_2$

Integrated System:

In one embodiment of this invention, the hydride would be stored in one vessel and the hydrogen generation modulated by adding or removing energy to the system (heat, pressure, friction, etc). Because the H2, by a large extent, would not be preferentially bonded onto the adsorbent media, it will remain at the headspace of the container. Whenever the gas is vented out, most of the headspace gas will be extracted out (namely H2). Any hydride accidentally removed together with the gaseous H2 can be filtered out of the stream using a membrane or chemical filter.

In another embodiment, hydride storage and decomposition occur in two separate medias. The first material would consist of an adsorbent as described in section (A). The second stage, stored in a separate vessel or in a separate partition, will contain a catalyst that decomposes the hydride into a solid and hydrogen gas (as described in section B). As with the previous embodiment, hydrogen gas will be separated from the remaining hydride gas using membranes or filters. The preceding considerations suggest the following conceptual configuration (Figure 2). Hydride gas transfer from storage to decomposition vessels will be controlled using a venturi or mechanical pump.

Membranes will operate based on molecular size or polarity. For instance, Nafion membranes have been known to separate gases based on these characteristics. Check valves pressure switches and/or mechanical regulators can be used throughout the system to prevent backflow and to control generation of hydrogen and to ensure safe operation. In addition, hydrogen sensors can be integrated inside and outside the system to monitor generator performance and for safety purposes.

Materials Proposed:

The hydride materials proposed for this invention must generate hydrogen upon decomposition. Preferably, the by-products should be in the solid phase and regenerable back to their hydride form. Optimum materials should form multiple H2 molecules for every parent hydride; at the same time, toxicity and reactivity of the hydride and its by-products should be minimized. A final consideration for extensive world-wide use is availability. The following are a few candidates:

For example, silane can be adsorbed at ambient pressure on ATMI, high capacity carbon monoliths at a level of 140g/L. Assuming stoichiometric decomposition, the amount of silane necessary for 4.5% hydrogen storage is 286 g/L. Hence current materials can already achieve approximately 50% of the 2005 DOE hydrogen storage capacity at ambient pressure. The advantages offered by silane (e.g., it is a commodity chemical, less toxic than the other candidate compounds, and capable of safe delivery), far outweigh its disadvantages. Disilane or higher-order silanes can also be used.

Ammonia is readily used in industrial processes. Compared to silane, hydrogen yield is lower but it is less reactive. The by-product is safe N2 that can be easily separated from hydrogen. Decomposition of ammonia into N2 and H2 is not trivial (from the energy point of view) and catalysts may be required.

Boranes (diborane, penta-borane, deca-borane) are great potential sources of H2. Upon decomposition, they form boron metal that can be oxidized or re-hydrided.

Hydrocarbons: Readily available and may contain plenty on H atoms. Decomposition to carbon is likely to require a catalyst and energy (similar to ammonia). Regeneration may be difficult if stored in a carbon matrix as the by-product is the same as the adsorbent.. Using a different adsorbent (such as a zeolite) may prove beneficial.

In gas storage operations, one downside is the continual decomposition of the silane or germane gas to hydrogen and silicon/germanium during storage even AT ROOM TEMPERATURE. It now appears that this downside could be turned into upside potential by offering this system as a hydrogen source. The prime novelty of this discovery being its ability to supply hydrogen gas continually at room temperature until the silane is fully decomposed.

Experiments conducted recently reveal that silane decomposition with formation of hydrogen gas can be either suppressed or enhanced depending upon which doping agent is applied to the carbon prior to gas storage (Fig. 1). Even more important is evidence that the decomposition continues, even years after initial storage (Fig. 2).

A 100 gram sample of carbon (perhaps only 100 cc volume) carrying an adsorbed phase of 22 grams of silane could generate 30.8 liters of hydrogen gas when the silane is fully decomposed. Decomposition rates can be adjusted by impregnating the carbon with various dopants. Boric acid dopant, for example, reduces the rates of decomposition dramatically while phosphoric acid doping of the carbon prior to adsorption of the silane gas has been shown to double the rate of hydrogen production over that of the un-treated carbon, all at room temperature.

What is proposed then is a light-weight, small volume, gas storage container rated to ~50 psig, comprising silane gas, SiH_4, at sub-ambient pressure, adsorbed on an activated carbon which has been doped with a doping agent such as phosphoric acid to accelerate silane decomposition. The gas dispensing mechanism would incorporate a selective hydrogen separation membrane to prevent discharge of silane gas but allow hydrogen flow to a small, portable fuel cell. An infantryman carrying the hydrogen-supply device incorporated into a small fuel cell system would have electric power to continually charge a small battery system. By careful selection of carbon selection, and carbon treatment, hydrogen rates could be designed to match the hydrogen demand of the fuel cell thereby maximizing the life of the hydrogen supply.

When the gas source has been fully discharged, the cylinders could be opened to the atmosphere allowing silicon oxidation to environmentally benign silica before disposal.

Silane gas is not only toxic but also pyrophoric and its accidental release could be problematic. By supplying the gas at sub-atmospheric pressure these concerns are partially alleviated. Even so, an infantryman would be expected to carry high explosive devices so the additional risk associated with carrying a silane source is probably small.

It is important to add that other metallic hydrides and organometallic hydrides are known to generate hydrogen on storage on a carbon adsorbent so the invention should not be limited to the use of silane and germane only.

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Attachment 1. Figures.

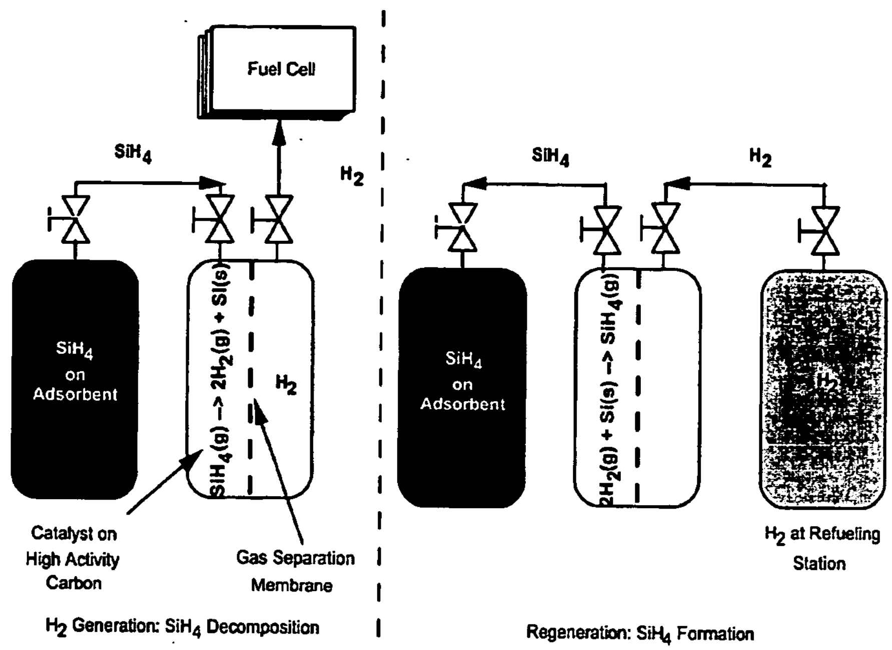

Figure 1. Conceptual schematic of hydrogen storage *via* silane adsorption, and regeneration.

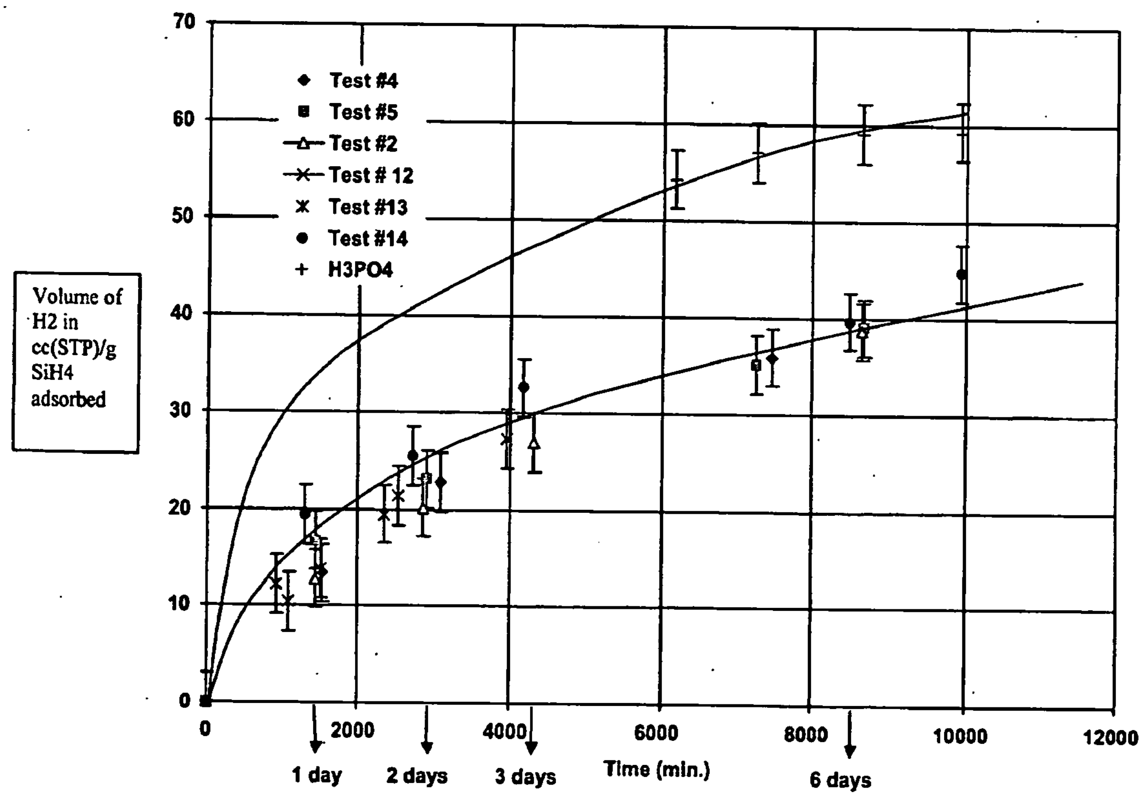

Figure 2. Silane decomposition to hydrogen and silicon on untreated carbon (various tests) and H_3PO_4-treated carbon. Note: this was a study of undesirable decomposition during storage. Much faster rates can be expected using optimized decomposition catalysts.

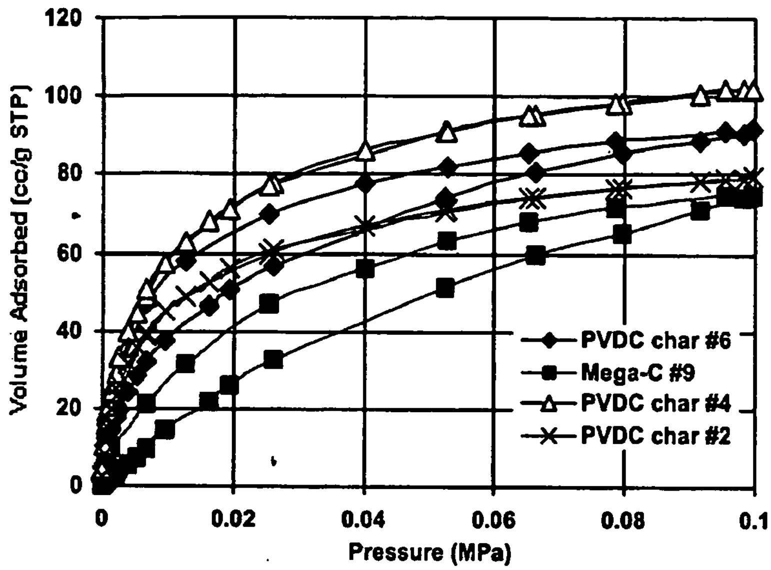

Figure 6. SiH_4 isotherms at 294.2K.

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